Lab: Thermodynamics of Saturated Borax Solutions

Background: Borax is commonly called sodium tetraborate decahydrate and has the formula $Na_2B_4O_7 \bullet 10H_2O$. However, based upon its chemical behavior as the sodium salt with the conjugate base of weak boric acid, a more descriptive formula for borax is $Na_2B_4O_5(OH)_4 \bullet 8H_2O$, also called tincal. Borax dissolves and dissociates in water according to the equation below:

$$Na_2B_4O_5(OH)_4 \bullet 8H_2O(s) \Leftrightarrow 2Na^+(aq) + B_4O_5(OH)_4^{2-}(aq) + 8H_2O(l)$$

At equilibrium, the solubility-product constant for borax is determined by: $K_{sp} = [Na^+(aq)]^2\,[B_4O_5(OH)_4^{2-}(aq)]$

The borate ion, $B_4O_5(OH)_4^{2-}(aq)$, can accept two protons from a strong acid in an aqueous solution. Therefore, the molar concentration of the borate anion in a saturated solution can be determined during a neutralization titration with standardized hydrochloric acid. The concentration of the sodium ions in the saturated solution will be twice the molar concentration of the borate ions.

The free energy of the dissolution of borax is related to the equilibrium constant by the equation:

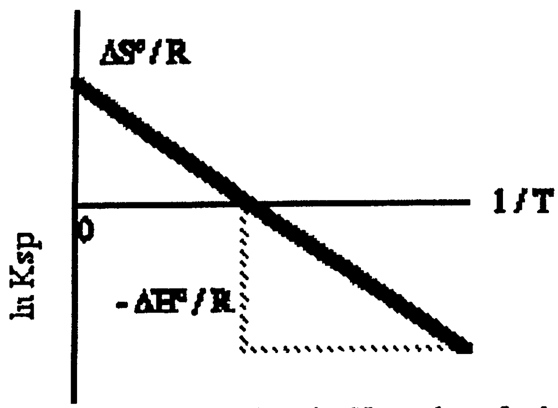
$\Delta G° = -RT \ln K_{sp}$, where $R = 8.314 \times 10^{-3}$ kJ/mol•K and T is the Kelvin temperature

The free energy is also related to the changes in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) by the equation:

$$\Delta G° = \Delta H° - T\Delta S°$$

Setting these two free energy equations equal to each other gives the expression: $-RT \ln K_{sp} = \Delta H° - T\Delta S°$

Re-arranging and solving for the $\ln K_{sp}$ results in an equation in the form of a linear relationship, $y = mx + b$. By plotting a graph of $\ln K_{sp}$ versus $1/T$, the slope of the line equals $-\Delta H°/R$ and the y-intercept equals $\Delta S°/R$.



$$\ln K_{sp} = -\frac{\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R}$$

$$y = m\,x + b$$

Problem: Can you determine the K_{sp} values for borax at various temperatures, then use this information in order to determine the free energy, enthalpy and entropy changes for the dissolution of solid borax?

Procedure:

1. Fill a 50 mL buret with standardized ~0.5 M HCl(aq). Record the exact molarity of the acid.

2. Saturated borax solutions must be prepared at six different temperatures, ranging from 0°C to 60°C. The amount of borax that will dissolve before the solution becomes saturated will increase with increasing temperature. The following chart indicates the approximate mass of borax needed to completely saturate 100 mL of distilled water at the various temperatures.

Temp °C	0	20	30	40	50	60
g borax	5	9	12	16	23	34

   Prepare one of the saturated solutions, as assigned by your instructor, by adding the mass of borax to 100 mL of distilled water in a 125 mL Erlenmeyer flask. Place the flask in a 400 mL beaker filled with water heated to ~5°C higher than your assigned temperature. (For the 0°C trial, allow the solution to set at room temperature.)

3. After 5 minutes of heating, remove the flask from the water bath, stopper it and shake for 2 minutes. Remove the stopper and return the flask to the water bath. Allow the water bath to cool down to your assigned temperature and for the borax solution to reach thermal equilibrium. After another 5 minutes, stopper the flask and shake for 2 minutes again, then return it to the water bath. There should be some solid remaining that will settle to the bottom of the flask. Allow the borax to settle until the solution is clear. The solution is now saturated.

4. Prepare a sample of a saturated borax solution for analysis by using a volumetric pipet to remove 5.00 mL of the solution and transfer it to an Erlenmeyer flask. (*Do not* transfer any of the solid borax!) Record the *exact* temperature of the saturated solution used. Rinse the pipet three or four times with warm distilled water and combine the washings with the sample.

5. Add 1 mL of bromocresol green indicator to the flask and titrate with the standardized HCl until a yellow-colored endpoint is reached. (The indicator is yellow at a pH < 4.0 and blue at a pH > 5.6. A green color is present within this pH range.)

6. Complete the HCl titration using samples from each of the six saturated solutions prepared.

Results & Calculations:

1. Calculate the molar solubility of borax at each of the measured temperatures.

2. Calculate the solubility-product of borax at each of the measured temperatures.

3. Plot the natural logarithm of the solubility-product versus the reciprocal Kelvin temperature for each sample and draw the best-fit straight line through the data points.

4. Determine the slope of the linear plot and calculate the standard enthalpy of solution for borax.

5. Determine the y-intercept (at $x = 0$) of the linear plot and calculate the standard entropy of solution for borax.

6. Calculate the standard free energy change for the solution of borax.